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ALKALI HALIDES COLORED BY COLLOIDAL METAL

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Alkali halides colored with an excess of alkali metal develop absorption bands
due to colloidal metal upon moderate heating, provided the concentration of alkali
metal is above the stable concentration of F-centers at the treatment temperature.
The extinction is due almost entirely to absorption, rather than scattering, unless
the particle size is greatly increased by extended treatment. The location of the
band maxima in NaCl, KCl, KBr, and KI can be satisfactorily calculated from the optical
properties of the metal. The particle size range for the smaller particles is within the
limits 10 Å - 50 Å. The heat of dissociation of colloid in the four lattices is
calculated. A new band in KI which has many characteristics of a colloidal band, but
which absorbs in a region far from that calculated for colloidal potassium is described.

I. Introduction

There has been much recent interest in the coloring of alkali halide crystals
by irradiation with x-rays, bombardment by high energy particles, or by heating in the
vapor of an alkali metal[1]. At moderate temperatures, the color centers produced are

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(1) N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals", Oxford (1948)

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unstable with respect to centers which can be described as "colloidal", and a study
of the nature of the colloidal centers and their equilibrium with the smaller color
centers is desirable in completing the outlines of the theory of ionic solids.

The occurrence of similar colloidal metal dispersions is encountered in the
electrolysis of fused salts, in natural blue rock-salt, in certain colored glasses
such as gold ruby glass, and in silver halides which have undergone prolonged

irradiation as in the "print-out effect". In the alkali halides, the colloidal centers are most conveniently prepared by warming crystals containing F-centers in excess of the stable concentration and allowing the centers to coagulate. Since crystals colored by irradiation contain an equal number of F-centers and holes, a competing reaction, namely recombination of the electrons and holes, makes the formation of colloid unlikely; for this reason it is necessary to use crystals which have been additively colored by heating in an alkali metal vapor and rapidly quenched to room temperature to "freeze in" a high concentration of color centers.

The colloidal centers cause strong absorption in a narrow spectral region, and, unless the particle size is greatly increased by prolonged heating, very little light scattering is observed[2]. The absorption band will be referred to here as the

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(2) R. W. Pohl, "Einfuhrung in die Optik", Springer, Berlin (1943)

"colloidal band".

II. Properties of Colloidal Centers

(A) Absorption of Light

The shape and location of the absorption band for small spheres of metal, of diameter much less than the wave length of the incident radiation and imbedded in a medium of refractive index n_u, can be calculated from the equation[2]:

$$K = \frac{36\pi N_v V \frac{n^2 k}{n_u}}{\lambda \left[\left(\left(\frac{n}{n_u}\right)^2 + \left(\frac{nk}{n_u}\right)^2 \right)^2 + 4 \left(\left(\frac{n}{n_u}\right)^2 - \left(\frac{nk}{n_u}\right)^2 + 1 \right) \right]} \tag{1}$$

Where K is the extinction coefficient defined by

(path length) K = 2.303 (optical density),

N_v is the number of particles per unit volume, V is the volume of a single particle, λ is the wave length in air for which K is sought, n is the refractive index of the metal, and nk is the "absorption coefficient" defined by

$$nk = K\lambda/4\pi.$$

Pohl describes the application of (1) to the colloidal sodium band in NaCl. Since neither N_v or V are known, the maximum value of K was set equal to the empirical value; the location and shape of the band then agreed quite well with the observed location and shape. This is evidence that the centers in NaCl are very small and can be treated as spheres. It may be also considered proof that when several F-centers coagulate, an equal number of surrounding cations are discharged so that the product is in actuality a metal speck.

For the alkali halides, in the spectral region of interest, n is very small compared to nk. This allows an easy calculation of the location of the band maximum by neglecting the terms in the denominator of (1) and obtaining the condition for which the denominator vanishes, namely

$$nk = \sqrt{2} \cdot n_u$$

Since neither nk nor n_u changes much with temperature, and the absorption is not influenced by lattice vibrations, neither the band maximum nor the breadth of the band should be altered by changing the temperature of observation of the band. This has been confirmed by experiment[2,3], and temperature insensitivity sometimes has

(3) A. B. Scott and W. A. Smith, Phys. Rev., **83**, 982 (1951)

been regarded as a sufficient criterion for a colloidal absorption band. We later present evidence to show that it may not be sufficient.

(B) Particle Size

By prolonged heating, or increasing the treatment temperature, colloidal particles in NaCl may be converted into larger particles[4,5] which may be detected

(4) E. Mollwo, Nachr. Ges. Wiss. Gottingen II, 254 (1932)
(5) M. Savostianowa, Z. Physik, **64**, 262 (1930)

ultramicroscopically. The smaller colloidal particles cannot be detected in this way.

Experiments have recently been performed in this laboratory to establish the presence of the smaller particles, exhibiting a strong colloidal band in KCl, by the use of the electron microscope. Surface replicas in collodion were made of freshly cut crystals of stock KCl, crystals containing F-centers, and those containing colloidal centers. The replicas were shadow cast by chromium and examined at a magnification of 16,000 X. The resolving power was about 50 $\overset{\circ}{A}$. In no case was there an observable difference between the surfaces of the three categories. This means that the colloidal particles, which should leave pits or mounds of K_2O on the interior surface of a cloven crystal, are smaller than about 50 $\overset{\circ}{A}$ in diameter, and contain less than 10^3 potassium atoms.

For concentrations of alkali metal less than 10^{18} atoms/cc, the shape and location of the colloidal band in KCl, KBr, and KI is fairly independent of temperature of formation and treatment time. Thus it may be concluded that we generally are dealing with particles below the limit of detection of the ultramicroscope or electron microscope.

(C) Photoconductive Properties

In contrast to crystals containing F-centers, which become conducting when illuminated by light absorbed by the F-centers, crystals containing colloidal alkali metal conduct when illuminated with light of wave length well removed from the absorption region. In colloidally colored NaCl, for example, the maximum photocurrent is produced by 370 mμ light, while the maximum absorption is at about 550 mμ.[6]

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(6) Z. Gyulai, Zeitx. f. Physik 35, 411 (1936)

The curve of current plotted against wave length is very similar to that for the photoelectric current from clean sodium surface, but is displaced by 0.5 eV in the direction of lower energy. This result has been interpreted[1] to show that the energy of an electron in conduction band in NaCl lies about 0.5 eV below that of an electron

immediately outside the crystal.

Further experiments on the photoconduction of alkali halides containing colloidal metal would be very useful in detecting the presence of colloidal centers in the presence of other centers (R_1, R_2, and M) which absorb in the same region. The photocurrent maxima should be well separated even though the absorption curves overlap. Such experiments are now being started in this laboratory, with the hope of shedding light on the centers responsible for the R'-band[7].

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(7) A. B. Scott, L. P. Bupp, and H. J. Hrostowski, Phys. Rev., 79, 346 (1950)

(D) Equilibrium with F-centers

The experiments described so far may be interpreted to show that the centers responsible for the colloidal band are metallic, more or less spherical, and in the usual case are too small to be observed by light-scattering methods. No lower limit has been set upon their size, other than that enough atoms must be included in each center so that the optical properties of the center are essentially those of the metal in bulk.

Further information about the lower limit may be obtained from a study of the thermal equilibrium between the "atomically" dispersed F-centers and the colloidal centers. A detailed study of this equilibrium in KCl has been reported[3]. Using the same procedure, a study of the equilibrium in KBr, KI, and NaCl has now been completed.

In all four alkali halides the equilibrium has been found to be heterogeneous; the concentration of F-centers in equilibrium with colloidal centers at any temperature is independent of the total concentration. In Table I[8] are reported the concentrations

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(8) From the Ph.D. thesis of William A. Smith and the M.S. thesis of Milton A. Thompson, Oregon State College,(1953)

TABLE I

EQUILIBRIUM CONCENTRATION OF F-CENTERS IN ALKALI HALIDE CRYSTALS CONTAINING COLLOIDAL METAL

Crystal and Range of Total Concentration, atoms/cc.	Temp., °C.	No. of Observations	Ave. F-center Conc. x 10^{-16} per cc.
KCl	300	7	11.0
18 - 100 x 10^{16}	350	6	19.0
	400	8	29
	450	8	64
KBr	230	9	5.4
11 - 70 x 10^{16}	283	4	10.6
	309	18	15.0
	318	5	17.4
	340	8	25
	350	4	31
KI	303	5	9.0
19 - 52 x 10^{16}	323	9	11.6
	350	5	17
	372	10	20
NaCl	450	8	2.4
4 - 12 x 10^{16}	490	15	4.2
	525	13	4.6
	600	6	6.0

of F-centers in equilibrium with colloidal centers for several temperatures in KBr, KI, and NaCl. Data for KCl is included for comparison. Each of the concentrations listed is the average of four or more independent measurements. The accuracy of the measurements is, in the case of KBr and KI, comparable to that in the case of KCl. Greater uncertainty exists in the value for NaCl since the equilibrium concentration even at the higher temperatures is relatively small, and during quenching from higher temperatures more coagulation can occur.

As anticipated, the stability of the F-centers is about the same in the three potassium salts, but much lower in NaCl, at any temperature, since it is determined primarily by the vapor pressure of the colloidal metal. The same results were obtained when KCl was colored with Na vapor as when it was colored with K vapor, so that no matter what alkali metal originally furnished the excess electrons, the colloidal metal is produced from the cation of the lattice.

If the colloidal centers contain as few as 10 atoms, doubling the total concentration would cause an increase in F-center concentration (at the lower temperature where the F-center stability is small) of about 7%. Since this change could be just detected by the analytical methods used, and since no appreciable change was noted with change in total concentration, 10 atoms may be taken as the lower limit of size for the colloidal particles, as set by the study of the F-center stability; the equilibrium is thus adequately described as heterogeneous, and the fact that the metal centers act as a separate phase is justification for the term colloidal.

The smaller colloidal particles may now be safely assumed to contain between 10 and 10^3 atoms and have a diameter between 10 and 50 $\overset{\circ}{\text{A}}$.

The variation of F-center stability with temperature is shown for KBr in Fig. 1. Especially to be noted is the slight variability of the absorption maximum of the colloidal band at about 820 mμ for centers prepared at different temperatures.

(E) Heat of Dissociation of Colloid

The value of ΔH for the process colloid = F-center was reported to be 8.0 k cal/mole at 350° in KCl[3]. From the data of Table I, similar values were computed for the other salts, as follows:

$$KBr\ (325°) : 11.4 \pm 0.4 \text{ k cal/mole}$$
$$KI\ (340°) : 9.0 \pm 0.3$$
$$NaCl\ (490°) : 9 \pm 2$$

(F) Location of the Colloidal Band Maximum

Fig. 2 shows typical absorption curves for four alkali halides in which the equilibrium between F-centers and colloid has been developed. Though the wave length of maximum absorption of colloid is somewhat variable for each lattice, the values presented are representative of the many crystals studied. Using data of Ives and Briggs[9, 10] for nk of sodium and potassium extrapolated to longer wave lengths, and

(9) H. E. Ives and H. B. Briggs, J. Opt. Soc. Am., 26, 238 (1936)
(10) H. E. Ives and H. B. Briggs, ibid., 27, 181 (1937)

that of Gyulai[11] for n_u of the alkali halides, the following band maxima were calcu-

(11) Z. Gyulai, Z. Physik, 46, 80 (1928)

lated by the use of equation (2): NaCl: 518; KCl : 730; KBr: 760; and KI: 800 mμ. The agreement in all cases is very satisfactory and what disagreement exists may be ascribed to uncertainties in the extrapolation if Ives and Briggs' data, to the presence of M-centers, and to the occurrence of some light scattering.

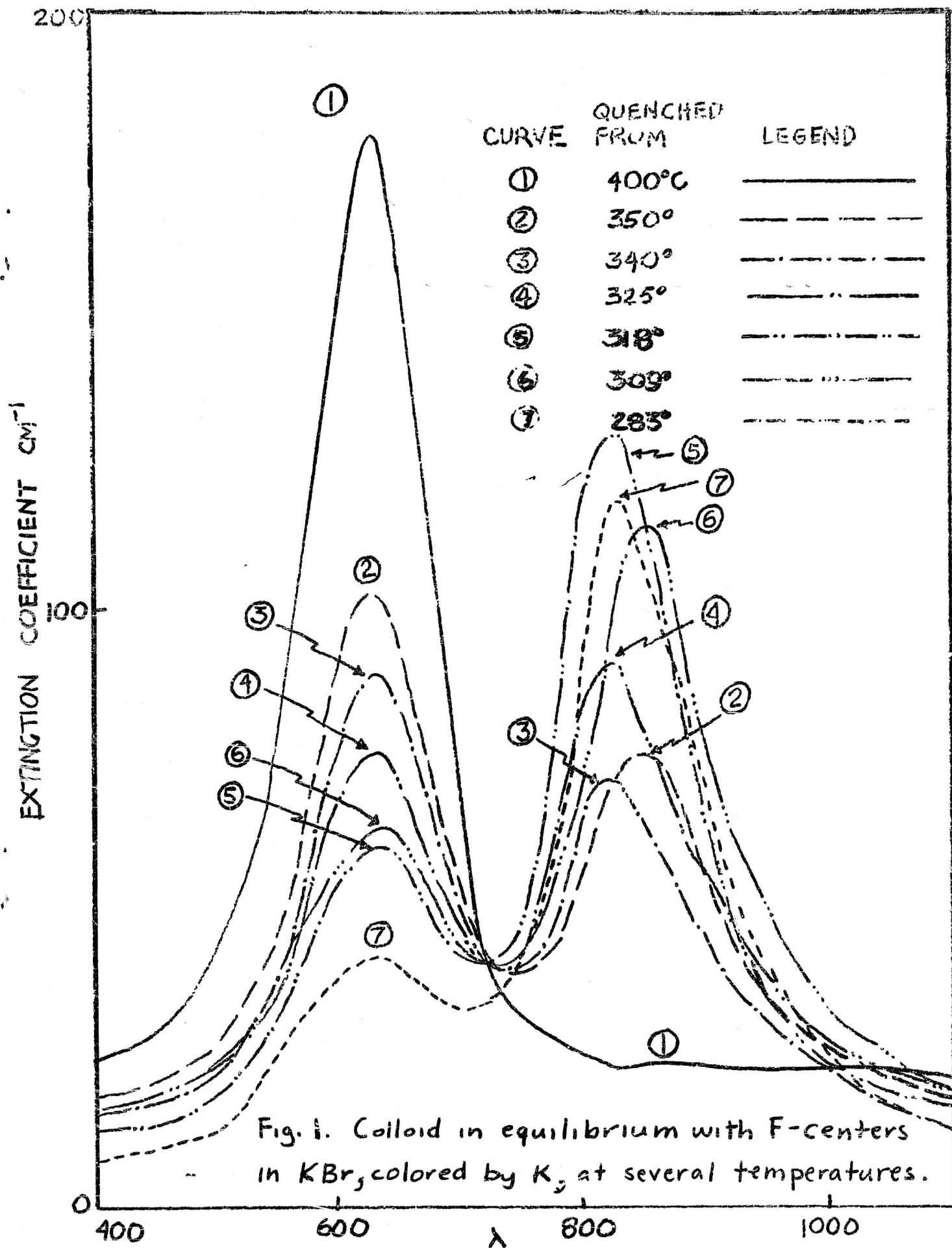### III. A New Absorption Band in Potassium Iodide[12]

(12) Reported in part at the Los Angeles meeting of the American Chemical Society, March 19, 1953.

In several crystals of KI, additively colored by heating for very long periods (more than 90 hours) at 600°, an unexpected absorption band was developed when an attempt was made to produce colloidal centers from F-centers. Upon heating such crystals at 275°, the F-centers are converted to centers absorbing at shorter wavelength. The maximum absorption of F-centers occurs at 695 mμ, and the new band had a maximum at about 650 mμ, the location varying somewhat from crystal to crystal. The new band was developed only in crystals of relatively low concentration of centers ($< 2.25 \times 10^{17}$/cc.)

The 650 mμ band was not appreciably affected by illumination with light absorbed by the band and the shape and location of the band was not altered by observing the band at liquid nitrogen temperature. Increase in temperature favors the reconversion of the centers to F-centers, as is shown by Fig. 3. A crystal containing the 650 mμ band developed at 275° was heated at 300° and then at 328°. The location of the band shifted continuously toward the location of the F-band. Illumination of crystals having absorption maxima intermediate between 650 and 700 mμ resulted in some destruction of F-centers with a shift of the absorption maximum toward 650 mμ.

These observations all indicate that the centers responsible for this new band are colloidal; however, this conclusion is contradicted by the application of Equation (2) to KI, which gives 830 mμ as the location of the band maximum for arbitrarily small metal spheres. Further experiments, such as a study of the photoconductance of these centers, and a systematic study of the conditions responsible for their formation will be required before more can be said about their constitution. The possibility that the centers are special forms of colloid, such as filaments or plates, will also bear investigation.

Fig. 1. Colloid in equilibrium with F-centers in KBr, colored by K, at several temperatures.

The figure axes: vertical axis "EXTINCTION COEFFICIENT CM⁻¹" marked at 0, 100, 200; horizontal axis "λ" marked at 400, 600, 800, 1000.

Legend:

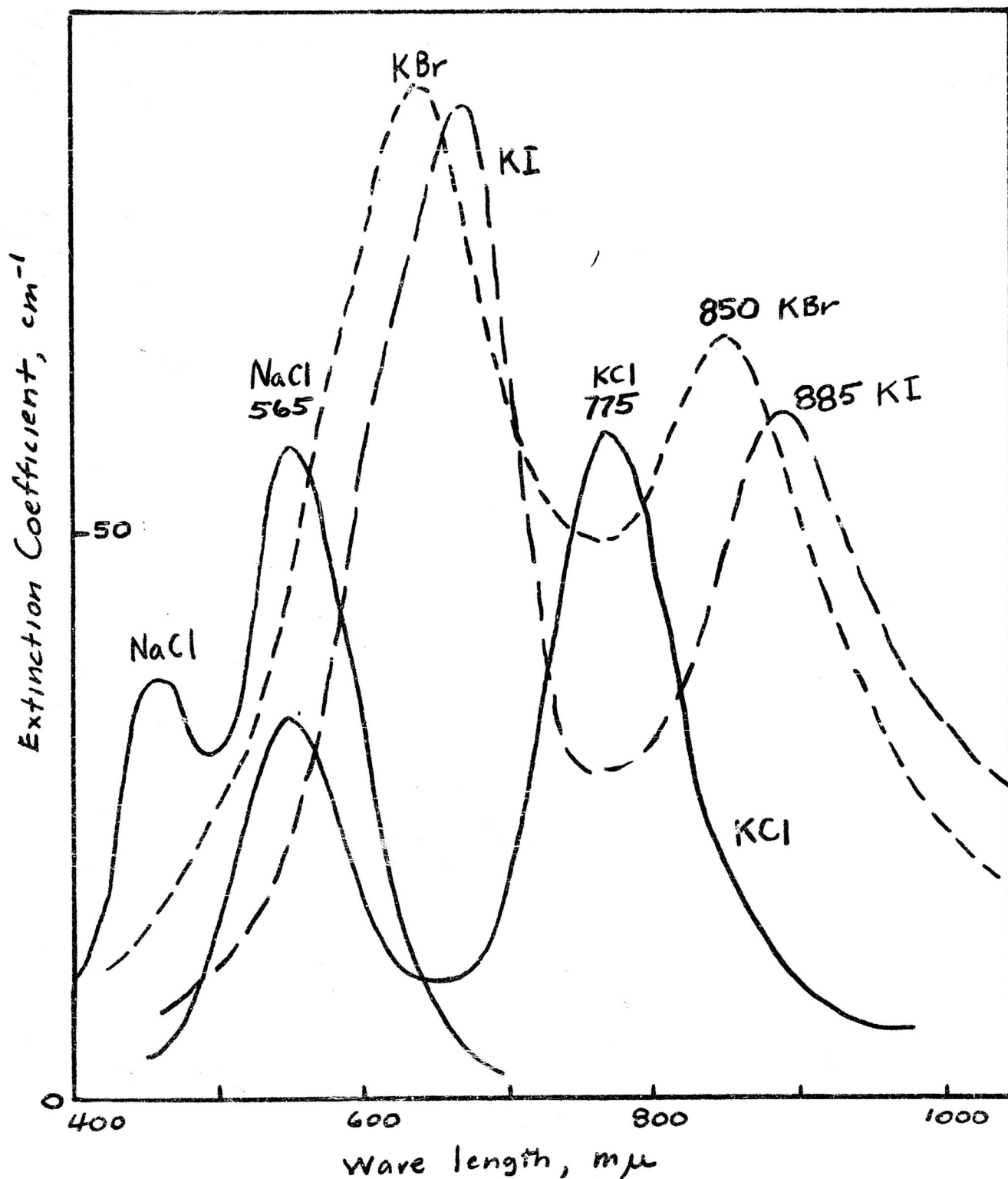| CURVE	QUENCHED FROM	LEGEND
①	400°C	
②	350°	
③	340°	
④	325°	
⑤	318°	
⑥	309°	
⑦	283°	

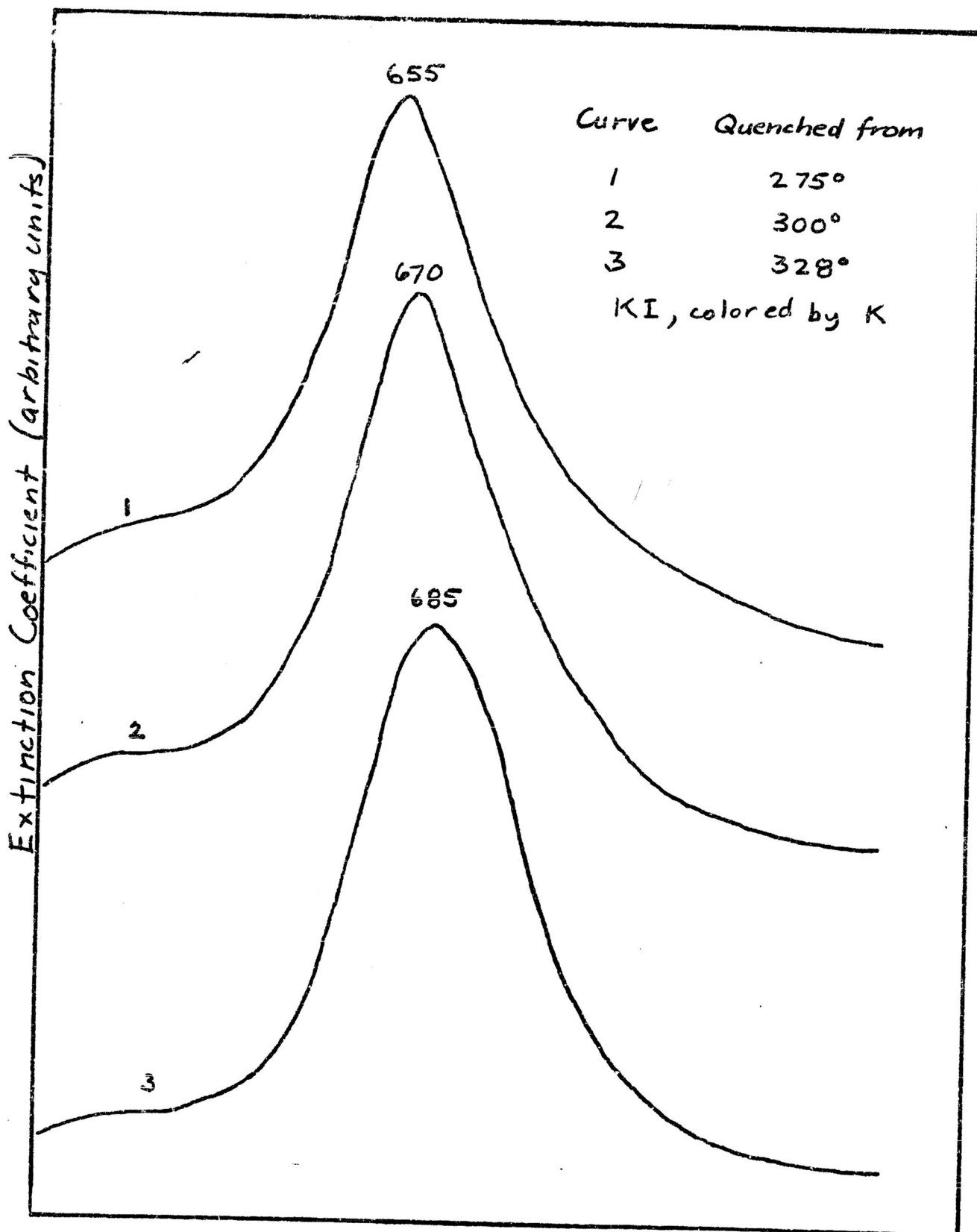Fig. 2 Colloidal Bands in four alkali halides.

Fig. 3 Dependence of band location on temperature of formation. Ordinates displaced vertically between curves.